Quantification of Nitrogen Forms in Argonne Premium Coals

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Abstract

X-ray Photoelectron Spectroscopy (XPS) was used to investigate the organic nitrogen forms present in fresh Argonne premium coals. In addition to the anticipated presence of pyrrolic and pyridinic nitrogen forms, a detailed analysis of the nitrogen (1s) line shape indicates the presence of quaternary type nitrogen species. A trend of decreasing level of quaternary nitrogen type with increasing coal rank is observed.

I. Introduction

The ability to quantify heteroatom functionalities in complex carbonaceous systems such as coal and petroleum residua can provide valuable insight into the organic macromolecular structure. Direct spectroscopic probes such as X-ray Photoelectron Spectroscopy (XPS) [1, 2] and X-ray Absorption Near Edge Structure (XANES) spectroscopy [3-7] have proven to be viable nondestructive techniques for organic sulfur speciation in non-volatile and solid carbonaceous materials. Results from these direct probes for organic sulfur have been compared to results based on pyrolysis methods [8]. XANES and XPS has been used to study the thermal chemistry of sulfur in coal [2] and these results provide insight into the transformations of organic sulfur that occur during pyrolysis based analytical probes. These results also provided insight into some of the processes at work during coal metamorphism [9].

A similar understanding of the chemistry of nitrogen in coal has not yet emerged. Progress has been made with XPS [10-14] and XANES [15] in the quantification of organic nitrogen forms. Development of both of these techniques is essential for a more complete understanding of chemical reactivity of coal. Mass transport of reactants and products is always a concern when dealing with coal. XPS has the advantage of being a probe the near surface (e.g. first 50 Angstroms) while XANES can derive its signal from the entire sample.

XPS methods have been widely used in the study of nitrogen forms in coal. Initial studies established that the energy position of the nitrogen (1s) signal was close to that expected for pyrrolic nitrogen [10,11]. It was possible to further curve resolve the XPS nitrogen (1s) spectra of coal into two peaks corresponding to pyrrolic and pyridinic types [10-13]. In a more recent study of a series of eight UK coals covering the range of 80-95 Wt% carbon it was found that the XPS nitrogen (1s) spectra could be curve resolved into two major components, pyrrolic and pyridinic [14]. The XPS sensitivity for nitrogen in this study was estimated at 0.1 atom % nitrogen and the total nitrogen content of the coals ranged from about 0.8 to 2.0 atom % [14]. In another recent XPS study of nitrogen, pyrrolic and pyridinic were the major forms identified in coal and its derived products with only minor unidentified components present in some samples at higher binding energy [13]. The first XANES studies of coal and petroleum asphaltenes supports the position that pyrrolic and pyridinic groups are the most abundant nitrogen forms in these materials [15]. An error estimate based on the unnormalized XANES nitrogen fraction, is considered to be about 10% [15].

A detailed analysis of the XPS nitrogen (1s) line shape has been used to quantify both the major and minor forms of nitrogen present in fresh Argonne premium coals. Changes in the distribution of nitrogen functionalities due to pyrolysis and hydropyrolysis have been examined for Illinois #6 bituminous and Wyodak subbituminous coal. The relevance of these results toward understanding coal metamorphism will be discussed.

II. Experimental

XPS spectra were obtained with a Vacuum Generators (VG) ESCA Lab system using MgK alpha non-monochromatic radiation and a either a single or a five channel detection arrangement. The five channel signal system provided a five times greater XPS signal for the same X-ray exposure time. The coal and model compound samples were made into fine powders and mounted to a metallic sample block by means of Scotch double sided non-conducting tape. An energy correction was made to account for sample charging based on the carbon (1s) peak at 284.8 eV. All spectra were obtained at an analyzer pass energy of 20 eV and a constant analyzer transmission mode. Under these conditions the full width at half maximum (FWHM) of 1.7 eV was obtained for the carbon (1s) spectrum of Argonne premium Pocahontas coal. The carbon (1s) line shape of Pocahontas coal is dominated by signal from hydrocarbons because of the very low total heteroatom content.

The nitrogen (1s) signal was curve resolved using a mixed Gaussian-Lorentzian line shape and a FWHM of 1.7 (eV). With these parameters it was possible to fit the nitrogen (1s) signal from pure model compounds, where nitrogen exists in a single chemical environment, with a single peak having these characteristics. The nitrogen (1s) spectra from coal were more complex. These spectra were curve resolved using the same theoretical line shape using peaks at 398.7, 400.2 and 401.3 ($\pm$0.05)(eV). These peaks correspond to the energy positions found for pyridinic, pyrrolic and quaternary type nitrogen functionalities respectively [13]. The peak shape and peak energy positions were fixed and only the amplitudes of these peaks varied to obtain the best fit to the experimental XPS data.

Elemental data for the coal samples were obtained from the Users Handbook for the Argonne Premium Sample Program [16]. Other elemental analytical data were obtained from Galbraith Analytical Laboratories, Knoxville, TN. Elemental data was also derived from XPS measurements from the areas of the XPS peaks after correction for atomic sensitivity. The sensitivity factors were obtained from VG sensitivity tables and experimentally measured standards. The elemental concentrations are presented relative to carbon.

Pyrolysis experiments were done in a quartz lined reactor in helium at 1 atm. The reactor temperature was raised to 400°C at approximately 0.5°C/sec. and held for 5 min. Under these conditions, little of the ultimate amount of hydrocarbons expected from the volatile matter determination are released while much of the oxygen as CO_2, H_2O and CO evolves [2]. Hydropyrolysis was accomplished in a closed reactor pressurized at room temperature to 70 atm. with a 95% hydrogen 5% helium mixture. The reactor temperature was raised to 427°C at a heating rate of 0.05°C/sec. and held for 30 min. These conditions favored the retention of coal hydrocarbon components and hydrocarbon products in the hydropyrolysis chars.

III. Results

The amount of nitrogen measured by XPS for the fresh coal samples was compared to bulk elemental data. The results are shown in Table I and there is excellent agreement for all coals except Illinois #6 and Lewiston coals. The generally good agreement indicates that there is no systematic enhancement or depletion of nitrogen at the coal surface. Illinois #6 and Lewiston coals gave lower nitrogen values with XPS. The origin for the difference with bulk value for these two coals is not yet resolved. The precise nature of the XPS results was demonstrated by numerous measurements on fresh coals of different particle sizes. The XPS nitrogen values for Illinois #6 coal were consistent throughout thermal and reductive treatment. Previous XPS investigations of other coal samples gave reasonable agreement between XPS and bulk values for nitrogen [10-14, 17, 18]. A tendency toward lower XPS values was noted [11, 13, 14] and a possible uncertainty in the XPS sensitivity factor for nitrogen was suggested as on possible cause for the discrepancy. This is a inadequate explanation in the present case of Argonne premium coals. Nevertheless, XPS has good precision for nitrogen quantification and the results are significant for identification of chemical changes in coal functionality.

The XPS nitrogen (1s) signals for the fresh Argonne premium coal samples is shown in Figure 1. Included in Figure 1 are the results of the curve resolution analysis for nitrogen forms. In each case the individual peaks and the total simulated spectrum are shown with the actual spectrum. The anticipated pyrrolic (402.2 eV) and pyridinic (398.7 eV) nitrogen forms were the most abundant species identified. The two forms could almost completely describe the nitrogen (1s) spectrum from a high rank coal such as Pocahontas, however, in all other cases it was necessary to include a peak for quaternary nitrogen ion (401.3 eV). Notice the relatively good signal to noise (S/N) characteristics of each spectrum and how well the sum of theoretical peaks fit the actual data. There are limited degrees of freedom in the curve resolution methodology, described in the experimental section. Data with good (S/N) provide a good test for the curve resolution methodology. Additional samples of fresh Argonne Premium coal were prepared, the XPS nitrogen (1s) signal recorded and curve resolved using the same methodology the gave essentially the same result, namely, that it was necessary to include in all cases a peak representative of quaternary nitrogen in addition to the ones representative of pyrrolic and pyridinic species. The estimated experimental precision for nitrogen forms is ($\pm$) 3.0 mole %.

The average numerical results of the curve resolution analysis are shown in Table 2. In all cases pyrrolic and pyridinic species are the dominant nitrogen forms in agreement with previous findings for coal [10-14], There is a significant contribution of quaternary nitrogen signal, especially in the lower rank Argonne premium coals. The data from each individual curve resolution analysis for nitrogen forms was plotted as a function of the weight % carbon in coal. Figure 2 shows these results. The solid and open points were obtained using a five and a single channel detection system respectively. These results show a distinct trend of decreasing relative amount of quaternary nitrogen with increasing coal rank for Argonne premium coals. A distinct trend for the relative level of pyrrolic nitrogen is not evident but there appears to be a tendency for the relative level of pyridinic nitrogen to increase with increasing coal rank.

The changes in the total level of organic nitrogen and oxygen following pyrolysis and hydropyrolysis of Illinois #6 and Wyodak coal were examined. The results of total nitrogen in the residual pyrolysis and hydropyrolysis chars are shown in Table III along with the results for total organic oxygen based on XPS analysis. For Illinois the level of organic oxygen drops nearly in half during hydropyrolysis. Less organic oxygen is lost during pyrolysis. There is only a slight increase in the relative level of total nitrogen after pyrolysis and hydropyrolysis. For Wyodak coal the organic oxygen level drops in half after pyrolysis and to one third of its initial value after hydropyrolysis. In contrast the relative level of nitrogen remain close to the initial value. The loss of organic oxygen after mild pyrolysis and hydropyrolysis conditions employed here is likely a result of loss of organic oxygen functionalities as CO_2, H_2O and CO [19, 20]. The loss of nitrogen as small gaseous molecules (i.e. NH_3, HCN, etc.) does not occur at low temperature ($T<450°C$) [21] prior to the devolatilization of hydrocarbons. Since some carbon is lost with CO_2 and CO as well as through formation of small quantities of methane or other small hydrocarbon gases a slight increase in the level of nitrogen relative to carbon would be expected if nearly all of the initial nitrogen is retained in the pyrolysis and hydropyrolysis chars.

The changes in the XPS nitrogen (1s) line shape following mild pyrolysis and hydropyrolysis of Illinois #6 and Wyodak coal have been studied. Figure 3 shows the The XPS nitrogen (1s) signals following hydropyrolysis. Included in Figure 3 are the results of the curve resolution analysis for nitrogen forms. In each case the individual peaks and the total simulated spectrum is shown with the actual spectrum. The anticipated pyrrolic (402.2 eV) and pyridinic (398.7 eV) nitrogen forms were the dominant species present. The two forms could describe the nitrogen (1s) spectrum following hydropyrolysis of Illinois #6 coal, however it was still necessary to include a small peak at the position expected for the quaternary nitrogen species.

The numerical results of the curve resolution analysis for nitrogen forms after pyrolysis and hydropyrolysis are shown in Table IV. There is a decline in the relative level of quaternary nitrogen for both coals after reaction. The decline is greater following hydropyrolysis. There is a significant increase in the relative level of pyridinic nitrogen for both coals after hydropyrolysis.

IV. Discussion

Detailed analysis of the XPS nitrogen (1s) signal has been used to determine the relative level of nitrogen forms in fresh Argonne premium coal samples. In agreement with previous investigations of other coals [10-14] pyrrolic and pyridinic species were the dominant nitrogen forms. In all cases it was necessary to include a peak found at the position expected for quaternary nitrogen ion. The relative level quaternary nitrogen decreases with increasing coal rank. It seams plausible that the quaternary nitrogen ion is associated with oxygen and the observed functional trend is caused by the loss of organic oxygen functionalities during coal metamorphism.

Quaternary nitrogen species have been identified in the XPS nitrogen spectrum of derived products of coal quaternarized with methyl iodide and examples shown where quaternary nitrogen is the most abundant species [12, 13]. The presence of quaternary nitrogen forms in fresh coal samples has not been reported before. The estimated experimental precision in the present study Argonne premium coal samples is estimated at ($\pm$) 3 mole %. It is possible that quaternary nitrogen species in lower rank coals was not measured in previous studies because the confidence level in the curve resolution process was substantially poorer on the order of ($\pm$) 10 mole %.

The XPS analysis for nitrogen forms in pyrolysis and hydropyrolysis chars showed that the relative level of quaternary nitrogen declines following reaction and is accompanied by a decline in the relative level of organic oxygen. There is ample reason to believe that nearly all of the nitrogen initially present is retained in the coal chars after reaction. The preferential retention of nitrogen [22] compared to sulfur and oxygen [2, 19, 20, 22] has been noted before. In the case of hydropyrolysis chars the relative level of pyridinic nitrogen increases substantially. It is concluded that the quaternary nitrogen species present in Illinois #6 and Wyodak coal are associated with oxygen and that the associations are broken during reaction. Furthermore, it appears likely that the quaternary nitrogen species is transformed during reaction and is largely retained in the coal char as a pyridinic nitrogen form. The appearance of quaternary nitrogen in fresh lower rank coal and the partial retention of these forms after mild pyrolysis indicates that these represent a significant class of strong non-covalent interactions present in the macromolecular structure of coal.

A detailed analysis of the XPS nitrogen (1s) line shape indicates the presence of quaternary type nitrogen species in addition to the anticipated pyrrolic and pyridinic forms. A trend of decreasing level of quaternary type nitrogen with increasing coal rank is observed. The quaternary nitrogen species is lost with the loss of oxygen functionalities during pyrolysis. The ratio of pyridinic to pyrrolic nitrogen increases after pyrolysis. These observations suggest that the quaternary nitrogen species is associated with oxygen and that the association is broken as a result of thermal reactions. Furthermore, it appears that the quaternary nitrogen is transformed and remains in the coal char as a pyridinic nitrogen form.

V. Summary

Curve resolution analysis of the XPS nitrogen (1s) spectra of Argonne Premium coal showed that pyrrolic and pyridinic nitrogen are the most abundant forms. Quarternary nitrogen species are a significant fraction in lower rank coals and the trend is toward decreasing level of this species with increasing coal rank. Most nitrogen is retained in the remaining coal after mild hydropyrolysis. The relative amount of pyridinic nitrogen increases and while the level of quaternary nitrogen decreases after hydropyrolysis of Wyodak and Illinois #6 coal.

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Table I

Coal	Nitrogen/Carbon Total XPS	Atom Ratio (x100) Total Bulk
Beulah Zap	1.5	1.5
Wyodak	1.3	1.4
Illinois #6	1.2	1.7
Blind Canyon	1.6	1.7
Pittsburgh #8	1.2	1.3
Lewiston	1.0	1.7
Upper Freeport	1.5	1.6
Pocahontas	1.2	1.3

Table II

Coal	XPS Pyridinic	Mole Percent Pyrrolic	(± 3.0) Quaternary
Beulah Zap	26	58	16
Wyodak	25	60	15
Illinois #6	26	62	12
Blind Canyon	31	55	14
Pittsburgh #8	32	61	7
Lewiston	31	60	9
Upper Freeport	28	65	7
Pocahontas	33	64	3

Table III

Coal	XPS Atom Ratio (x100) Organic Oxygen/C	Organic Nitrogen/C
Illinois #6 (Initial)	9.0	1.2
Illinois #6 (Pyrolysis)	6.7	1.3
Illinois #6 (Hydropyrolysis)	4.8	1.5
Wyodak (initial)	16.9	1.3
Wyodak (Pyrolysis)	8.8	1.3
Wyodak (Hydropyrolysis)	5.6	1.4

Table IV

Coal	XPS Pyridinic	Mole Percent Pyrrolic	(± 3.0) Quaternary
Illinois #6 (Initial)	26	62	12
Illinois #6 (Pyrolysis)	30	64	6
Illinois #6 (Hydropyrolysis)	35	65	0
Wyodak (initial)	25	60	15
Wyodak (Pyrolysis)	29	62	9
Wyodak (Hydropyrolysis)	35	65	3

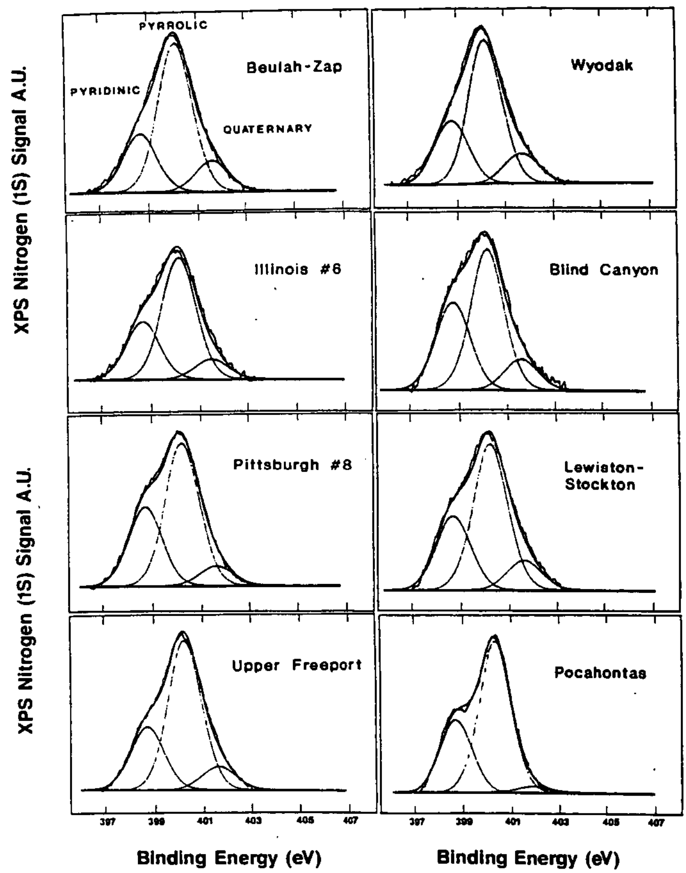

Figure 1. XPS Nitrogen (1s) Curve Resolution of Argonne Premium Coals

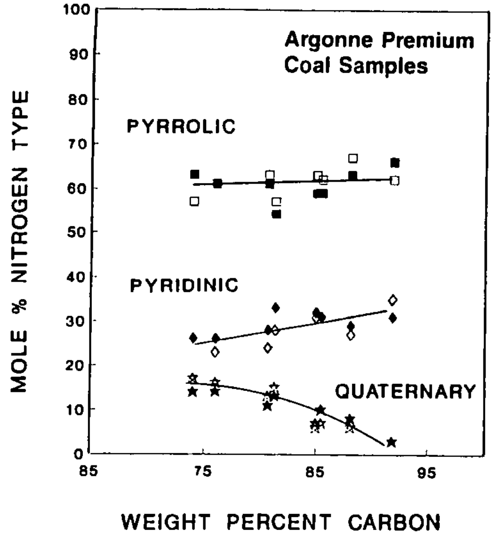

Figure 2. Nitrogen Functional Groups By XPS Curve Resolution Analysis

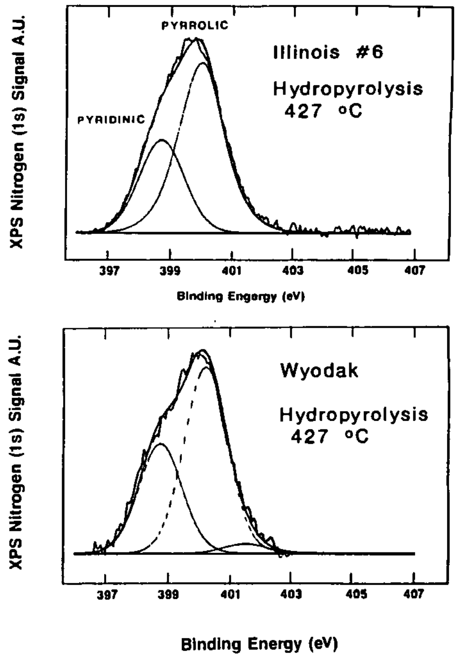

Figure 3. XPS Nitrogen (1s) Curve Resolution of Hydropyrolyzed Coals